

Local Bonding Arrangements in Amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$: The Importance of GE and TE Bonding

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14. ABSTRACT Studies of amorphous (a-) semiconductors have been driven by technological advances as well as fundamental theories. Observation of electrical switching [1], for example, fueled early interest in a-chalcogenides. More recently a-chalcogenides switching has been applied successfully to programmable memory devices [2], as well as DVD technology where the quest for the discovery of better-suited materials continues. Thus, switching grants researchers today with an active arena of technological as well as fundamental study. Bond constraint theory and rigidity theory provided a powerful framework for understanding the structure and properties of a-materials. Application of these theories to switching in a-chalcogenides holds the promise of finding the best composition suited for switching applications. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy [3] is an ideally suited technique to investigate the switching properties of these materials. Results of previous EXAFS experiments are presented and viewed through the lens of bond constraint theory and rigidity theory.					
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Local Bonding Arrangements in Amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$: The Importance Of Ge And Te Bonding

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Abstract. Studies of amorphous (a-) semiconductors have been driven by technological advances as well as fundamental theories. Observation of electrical switching [1], for example, fueled early interest in a-chalcogenides. More recently a-chalcogenide switching has been applied successfully to programmable memory devices [2], as well as DVD technology where the quest for the discovery of better-suited materials continues. Thus, switching grants researchers today with an active arena of technological as well as fundamental study. Bond constraint theory and rigidity theory provide a powerful framework for understanding the structure and properties of a-materials. Application of these theories to switching in a-chalcogenides holds the promise of finding the best composition suited for switching applications. Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy [3] is an ideally suited technique to investigate the switching properties of these materials. Results of previous EXAFS experiments are presented and viewed through the lens of bond constraint theory and rigidity theory.

1. Introduction

While many amorphous chalcogenide alloys are reported in the literature, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST) has received particular attention [4,5,6]. GST is a robust and reliable material for use in optical and electrical switching applications. While the compound's properties and performance are well documented [7,8,9,10], a fundamental explanation of the suitability of GST for these applications has not been identified. Bond constraint theory (BCT) [11,12] allows one to characterize the structure of various Ge-Sb-Te compositions, --or any amorphous network solid [13]-- across a spectrum from floppy to stressed-rigid. In the compositional range between these two regions, an intermediate phase exists where a balance is struck between entropy and enthalpy. Such a material, referred to as unstressed-rigid, may switch between a free energy minimum of an a-state to a second minimum of a c-state. Cyclability is assured as the material neither falls into an enthalpy driven trap of a crystalline state, nor does it slide down an entropy driven slope into an irretrievable amorphous state.

BCT couches the balance between stressed and floppy materials in terms of average number of constraints per atom in interatomic force field space and the number of degrees of freedom in real space (i.e. three.) Materials characterized by this condition are so-called "good glass formers." Local bonding configurations play a key role in the application of BCT. EXAFS spectroscopy, it seems, is ideally suited to compliment this requirement of BCT. In this paper, these two approaches are combined in order to gain insight into the optical memory material GST.

2. Experimental

GST films were RF sputtered onto aluminum foil substrates to a thickness of 2.7 μm . The samples were sliced into 10mm x 4mm sections and stacked, creating 8 layers with an effective film thickness of ~22 μm . EXAFS measurements of the K edges of Ge, Sb, and Te were taken in transmission mode using a Si(111) double-crystal monochromator at line ID-10 (MR CAT) of the Advanced Photon Source at Argonne

National Laboratory. Incident and transmitted photons were measured at room temperature with ionization chambers filled with Ar+15%Kr and Kr, respectively.

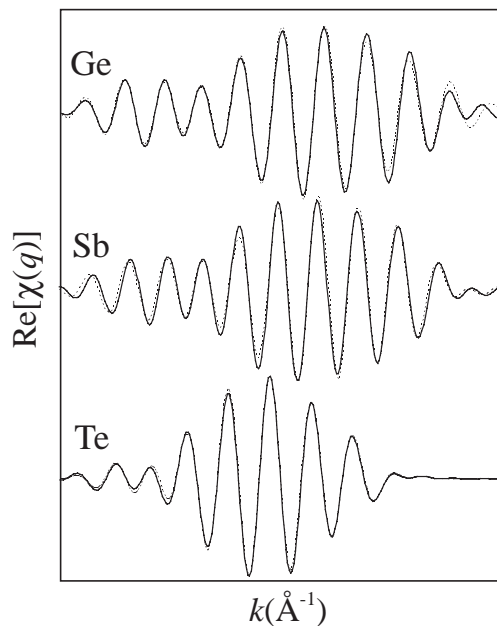


FIGURE 1. Plots of k^3 -weighted spectra for GST. Solid lines are data, dashed lines are fits.

Normalization and background removal of the data were performed using the Athena software package [14]. The k^3 -weighted Fourier transformed spectra were fit using the Artemis analysis package [14], which is based on the FEFF [15] and IFEFFIT [16] codes. A small molecular cluster molecular model with no periodicity was used as a way to avoid any bias toward crystallinity in the analysis. All three possible backscattering species were considered for each scattering atom, and of the six possible atom pairs, only three showed acceptable fits. Fig. 1 shows the fits in k space for all three edges.

Table 1 presents a summary of the coordination (N) and nearest neighbor distances for the four atom pairs, Ge-Te, Sb-Te and Ge-Ge. These results show internal consistency, within the error, for heteropolar bond lengths. Also note that the reported bond lengths agree with tabulated covalent radii for each species [17]. N determinations indicate fully coordinated Ge and Sb and slightly over-coordinated Te.

TABLE 1. Coordination numbers and interatomic distances for $\text{Ge}_2\text{Sb}_2\text{Te}_5$			
Atom	Bond	Coordination (N)	R(Å)
Ge	Ge-Te	3.9 ± 0.5	2.63 ± 0.01
	Ge-Ge	0.6 ± 0.2	2.47 ± 0.03
Sb	Sb-Te	2.8 ± 0.5	2.83 ± 0.01
	<i>Sb-Te(e)</i>	0.5 ± 0.3	2.51 ± 0.01
Te	Te-Ge	1.2 ± 0.3	2.62 ± 0.01
	Te-Sb	1.2 ± 0.3	2.83 ± 0.01

TABLE 1. Coordination numbers and nearest neighbor bond distances for a-GST as determined by EXAFS. Note the second, shorter Sb-Te distance labeled in italics as Sb-Te(e) indicating an electrostatic bond.

In the present case, similarities in photoelectron backscattering render it quite difficult, if not impossible, to differentiate between Sb-Sb bonds and Sb-Te covalent bonds using the EXAFS technique. Chemical preference, however, yields a guide for identifying the nature of the bonding environment. Bond energies for Sb-Te (40.6 kpm) and Sb-Sb (39.6 kpm) [18] support the interpretation that the Sb-Te bonds account for most, if not all, of the backscattering signal from the Sb atoms. The second, shorter Sb-Te distance is attributed to an electrostatic, or dative [19] bond between Sb and a positively charged three-fold coordinated Te atom.

The presence of homopolar Ge bonding suggests a model where virtually all Ge atoms are bonded to one Ge atom and three Te atoms in a Ge_2Se_3 type local bonding arrangement [20], as shown in Fig. 2. Sb atoms are then interspersed evenly throughout the structure with three Te neighbors in Sb_2Te_3 arrangements. The molecular structure of GST then includes the following local bonding arrangement: i) Sb_2Te_3 , ii) Ge_2Te_3 , and iii) three fold coordinated Te atoms, the nearest neighbors of which are Sb and Ge. In addition, the material includes dative bonds between positively charged three-fold coordinated Te, and pyramidal Sb groups that acquire a negative charge.

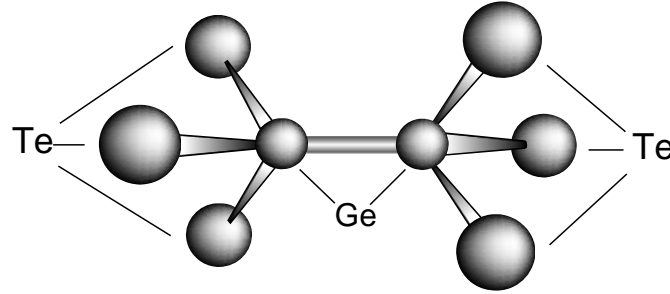


FIGURE. 2. Proposed Ge_2Te_3 configuration.

3. Bond Constraint Theory and Rigidity Theory

The physical requirement that the number of constraints in an amorphous material equals the number of degrees of freedom in the space that material occupies (or network dimensionality) defines a relatively simple criterion for an ideal, strain-free thin film or bulk material [10]. As the thin film materials addressed in this paper are neither i) one-dimensional or ii) two-dimensional and non-planar networks, the latter bond constraint metric is three, so that the average number of bonds/atom C_{av} is given in Eq. (1),

$$C_{av} = 3 \quad (1)$$

This equation is the basis for discriminating between materials with different degrees of ideality in the context of the “ease of glass formation”. When it is met, a material may be considered to be a “good glass-former.” BCT’s subtlety comes in determining the number of bonding constraints/atom in any given system.

For a system comprised of 2-, 3-, and 4-fold coordinated atoms with N atoms in its molecular formula, can be written in terms of the stretching and bending constraints, f_s and f_b , respectively. If n_r is the number of atoms with r -fold coordination in one molecular unit, it follows that

$$C_{av} = \frac{1}{N} \sum_{r=2}^4 n_r (f_s + f_b). \quad (2)$$

From this equation, it can be shown [10] that

$$C_{av} = \frac{5}{2} \langle r \rangle - 3. \quad (3)$$

The condition that a material be a good glass former expressed in Eq. (1) is then equivalent to the condition that the average coordination be given by

$$\langle r \rangle = 2.4. \quad (4)$$

An alternate approach that arrives at the same conclusion (Eq. 4) is given by rigidity theory. Developed originally by LaGrange and Clerk Maxwell, and later by Thorpe and co-workers [21,22,11], rigidity theory considers vibrational modes in systems with 2-, 3- and 4-fold coordinated atoms in a material with local molecular units of N atoms. In calculating the total number of modes of vibration of such a system, they identify modes that require energy (i.e. constraints) and those that do not. The latter are the so-called zero-frequency or *floppy modes*, given the symbol F . F can be expressed as the difference between the total possible number of vibrational modes of the system, $3N$, and the modes determined by constraint counting. Thus, F is given by

$$F = 3N - \sum_{r=2}^4 n_r \left(\frac{r}{2} + [2r - 3] \right). \quad (5)$$

The fraction of zero-frequency modes, $f = F/3N$ may then be calculated using Eq. (2) and Eq. (3), and is given by:

$$f = 2 - \frac{5}{6} \langle r \rangle. \quad (6)$$

With increasing average network coordination, the fraction of zero frequency modes decreases, and is exactly equal to zero at the condition given by in Eq. (4). The relationship between f and $\langle r \rangle$ is shown by the solid line of Fig. 3. The equivalence of the approach based on the assumption inherent in BCT (Eq. (1)) and the approach of rigidity theory (Eq. (6)) is manifest in the fact that each identify a material with $\langle r \rangle = 2.4$ as lying at a nexus dividing materials that are floppy from those that are stressed-rigid with respect to material properties.

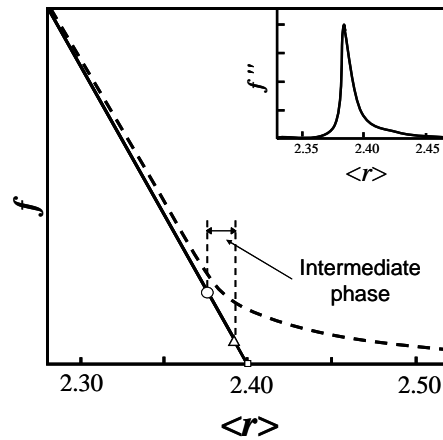


FIGURE 3. Plot of f as a function of $\langle r \rangle$. Theory shown by solid line and model shown by dashed line. Inset shows second derivative of f as a function of $\langle r \rangle$. Figure adapted from Ref. 11.

Beyond the simple analytical treatment outlined above, this research also includes computer modeling of large networks of atoms, providing a numerical determination of the fraction of zero-frequency modes, f [23]. Plots of f as a function of $\langle r \rangle$ reveal three distinct composition regions. One such plot for a system of 2-, 3-, and 4-fold coordinated atoms is shown as the dashed line of Fig. 3. A transition region is readily identified in a plot of the second derivative of f with respect to $\langle r \rangle$. This is as shown in the inset of the figure, and it identifies a narrow transition region, $2.37 < \langle r \rangle < 2.44$, between floppy and stress-rigid

regimes. The lower bound of this transition region represents the development of small and isolated pockets of rigid clusters, or *local rigidity*, the number of which increases as the average coordination increases. The upper bound indicates the percolation, or interconnection, of these locally rigid clusters, i.e., *global rigidity*, to generate a stressed-rigid material. For alloys with multiply-coordinated atoms such as $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$ numerical modeling efforts such as this clearly identify three types of material with different values of C_{av} : i) a floppy a material with low average coordination; ii) a stressed-rigid material with high average coordination; and iii) an intermediate-phase material near $\langle r \rangle = 2.4$ that is an ideal locally stressed material without percolation of stress, or *unstressed rigid*. Another study [24] identifies a similar region in the $\text{Ge}_x\text{Se}(\text{S})_{1-x}$ system, showing that GST is not the only system to exhibit this “intermediate phase” behavior.

4. BCT and EXAFS

Consider first the local bonding environment for Ge. The results in Table 1 give a total coordination for Ge of approximately four, an indication of tetrahedral coordination for all of the Ge atoms. To zeroth order, using Eq. (2), a tetrahedral Ge configuration yields $C_{av} = 7$, with five bending and two stretching constraints/atom. However, the combination of homopolar (Ge-Ge) and heteropolar (Ge-Te) bonds has a profound effect on constraint counting; bond-bending constraints can be removed by considering in detail the specific bonding configuration. In particular, bending constraints around each Ge atom are a mixture of Ge-Ge-Te and Te-Ge-Te motions. The force constant for the Ge-Ge-Te bending motion is significantly reduced with respect to that of a Te-Ge-Te bending motion due to the different Ge-Ge-Te and Te-Ge-Te bond energies. This permits the removal of 2.67 bending constraints (1.67 from two doubly-degenerate E-mode vibrations and 1 for a non-degenerate A-mode vibration) for the Ge_2Te_3 arrangement. Our results yield a bonding model in which all of the Ge atoms are in this configuration, thus the total number of bond-bending constraints around the average Ge atom are reduced from 5 to 2.33. This in turn reduces the total number of constraints for Ge atoms from 7 to 4.33.

In the Sb bonding environment, a three-fold pyramidal structure, there are 1.5 stretching constraints and 3 bending constraints, resulting in 4.5 total constraints. None of these constraints are broken; therefore, one finds the total constraints around the Sb atoms to be 4.5.

Table 1 indicates overcoordination of Te, which is supported by the following bond-counting exercise. The proposed model gives GST as a combination of Ge_2Te_3 and Sb_2Te_3 structural units. This counting results in a deficiency in Te for the GST composition, as stoichiometry requires that the addition of these two units equal $\text{Ge}_2\text{Sb}_2\text{Te}_6$. This 1/6, or ~17%, Te deficiency is reflected in our results, as the percent of over-coordinated Te determined from these fits is $0.4/2.4 \approx 17\%$. A Te deficiency, combined with full coordination of Ge and Sb require that some Te atoms over-coordinate, resulting in the presence of both two-fold and three-fold geometries. No constraints can be removed for the former configuration, and in the latter, constraints are removed, but proportionally so [25], resulting in 2 constraints for both configurations.

The total number of constraints for the entire GST alloy follows: Ge contribution: $4.33 \times 2 = 8.66$; Sb contribution: $4.5 \times 2 = 9$; Te contribution: $2 \times 5 = 10$. Thus,

$$C_{av} = \frac{8.66 + 9 + 10}{9} = 3.07. \quad (7)$$

This value of C_{av} is close the ideal value of 3 –and concurrently, via Eq. (3) $\langle r \rangle$ is close to ideal value of 2.4-- suggested for a material in the stress-free state, and more importantly, for a good glass former.

5. Summary and Discussion

EXAFS studies of the nearest-neighbor bonding of Ge, Sb and Te in as-deposited $\text{Ge}_2\text{Sb}_2\text{Te}_5$ films are presented. Analysis of the Ge K spectrum indicates significant concentrations of both Ge-Ge and Ge-Te bonds. Additionally, concurrent analysis of the three EXAFS spectra yields internally self-consistent atomic coordination numbers and bond lengths. Combined with bond-energies for the system, the EXAFS results give the following molecular structure: $\text{Ge}_2\text{Sb}_2\text{Te}_5 = \text{Ge}_2\text{Te}_3 + \text{Sb}_2\text{Te}_3$, with i) 17% of the Te-atoms 3-fold, rather than 2-fold coordinated, and ii) 20% of the Sb-Te atoms participating in electrostatic bonding to a nearby Te atom. The over-coordinated Te-atoms are assumed to have a positive formal charge of 1, and a subsequently smaller atomic radius, thereby accounting for the reduced distance associated with the Sb-Te dative bond. The average bond coordination, $\langle r \rangle$, and average number of bond-stretching and -bending constraints/atom, C_{av} , have been determined using bond constraint theory. The inclusion of Ge-Ge bonding in Ge_2Te_3 groups provides the microscopic basis for the good glass forming capability of GST and its propensity for repeatable phase change transitions.

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